

# Electrochemical properties of the carbon-coated $\text{LiFePO}_4$ as a cathode material for lithium-ion secondary batteries

Ho Chul Shin <sup>a,b</sup>, Won Il Cho <sup>b</sup>, Ho Jang <sup>a,\*</sup>

<sup>a</sup> Department of Advanced Materials Engineering, College of Engineering, Korea University,  
5-1, Anam-dong, Seongbuk-gu, Seoul 136-713, South Korea

<sup>b</sup> Battery Research Center, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, South Korea

Received 2 November 2005; received in revised form 20 December 2005; accepted 20 December 2005

Available online 20 February 2006

## Abstract

In this study the effect of the carbon coating on the electrochemical properties of  $\text{LiFePO}_4$  as a cathode for Li-ion batteries were investigated. The carbon-coated  $\text{LiFePO}_4$  particles were synthesized by the mechanochemical process and one-step heat treatment. Microscopic observations using SEM and TEM revealed that the carbon coating reduced the particle size of the  $\text{LiFePO}_4$ . The carbon-coated  $\text{LiFePO}_4$  showed much better performances in terms of the discharge capacity and cycle stability than bare  $\text{LiFePO}_4$ . It was confirmed that the carbon coating decreased the migration distance of Li-ion and enhanced the charge transfer from CV and ac impedance measurements. The improved electrochemical properties of the carbon-coated  $\text{LiFePO}_4$  were, therefore, attributed to the reduced particle size and enhanced electrical contacts by carbon.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Lithium iron phosphate; Carbon coating; Lithium-ion batteries; ac impedance

## 1. Introduction

Lithium iron phosphate ( $\text{LiFePO}_4$ ), since first proposed by Goodenough's group in 1997 [1], has been investigated as a viable alternative for a cathode material for lithium-ion batteries due to its large theoretical capacity ( $170 \text{ mAh g}^{-1}$ ), high safety, and low cost [2,3]. The  $\text{LiFePO}_4$ , however, has not been used as a commercial cathode material due to its low electrical conductivity ( $10^{-9}$  to  $10^{-10} \text{ S cm}^{-1}$ ) [4–7]. This is because the  $\text{LiFePO}_4$  has an ordered olivine structure, in which Li, Fe, and P atoms occupy octahedral 4a, octahedral 4c and tetrahedral 4c sites, respectively, and  $\text{FeO}_6$  octahedra are separated by  $\text{PO}_4$  polyanions.

Recently, several research groups made efforts to overcome this problem and showed possibility to overcome the limitation by coating  $\text{LiFePO}_4$  with carbon [8–11], doping transition metal ions [12–14], and reducing the particle size [15,16]. Ravet

et al. [8] reported that  $\text{LiFePO}_4$  showed a capacity close to  $160 \text{ mAh g}^{-1}$  at  $80^\circ\text{C}$  when it was coated with approximately 1 wt.% carbon. Yamada et al. [15] showed that good electrochemical performance ( $>95\%$ ,  $165 \text{ mAh g}^{-1}$ ) was possible even at room temperature by decreasing the particle size at moderate sintering temperatures ( $500\text{--}600^\circ\text{C}$ ). Huang et al. [10] fabricated carbon-coated  $\text{LiFePO}_4$  composites containing small (100–200 nm) carbon particles by mixing precursors with a carbon gel before sintering. This composite showed good rate capability and excellent cycle stability at room temperature. However, these synthesis routes were complicated and needed a sintering process at high temperatures for a long time. Franger et al. [17] and Kwon et al. [18] found that the mechanical alloying produced fine carbon-coated  $\text{LiFePO}_4$  particles and reduced the heat-treatment time.

In this study, the mechanochemical process was employed to synthesize the carbon-coated  $\text{LiFePO}_4$  using the precursor  $\text{Li}_2\text{CO}_3$  as a Li source and acetylene black as a carbon source. The emphasis of the current investigation was to find the underlying cause of the improvement of the electrochemical properties of the carbon-coated  $\text{LiFePO}_4$ . In order to examine the role of carbon on the electrochemical properties of  $\text{LiFePO}_4$  particles,

\* Corresponding author. Tel.: +82 2 3290 3276;

fax: +82 2 928 3584/3290 3704.

E-mail address: [hojang@korea.ac.kr](mailto:hojang@korea.ac.kr) (H. Jang).

analysis using XRD, SEM, TEM, EIS, and electrochemical tests were performed.

## 2. Experimental

$\text{Li}_2\text{CO}_3$  (Aldrich,  $\geq 99\%$ ),  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (Aldrich,  $\geq 99\%$ ), and  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  (Aldrich,  $\geq 99\%$ ) were used as starting materials. This mixture containing the precursors based on the stoichiometry of the compound was placed in a zirconia bowl and the mechanochemical activation was carried out using zirconia balls for 3 h using a planetary mill (FRITSCH Pulverisette 5) in the air. The rotating speed was 250 rpm and the ball-to-powder weight ratio was 20:1. The activated powders after the mechanochemical processing were heat treated at  $700^\circ\text{C}$  in an Ar + 5%  $\text{H}_2$  atmosphere in a tube furnace for 10 h. For the carbon-coated  $\text{LiFePO}_4$ , 5 wt.% acetylene black powders were added to the mixture of the starting materials. After the same mechanochemical treatment, the carbon-coated  $\text{LiFePO}_4$  powders were synthesized with the same heat-treatment conditions for the bare  $\text{LiFePO}_4$ .

After the heat-treatment, the gray (bare  $\text{LiFePO}_4$ ) and the black (carbon-coated  $\text{LiFePO}_4$ ) powders were furnace cooled to room temperature. The crystal structure of the bare and the carbon-coated  $\text{LiFePO}_4$  powders were examined by XRD analysis (RINT/DMAX-2500, RIGAKU/JAPAN). Surface morphology and particle size of the powder were analyzed by scanning electron microscopy (Hitachi S-4200) and HRTEM (FEI Technai/F20).

Cathodes were manufactured by mixing 85 wt.% of the prepared  $\text{LiFePO}_4$ , 10 wt.% acetylene black as a conductor, and 5 wt.% polyvinylidene difluoride as a binder. The mixture slurry was coated on an Al foil and dried at  $80^\circ\text{C}$  for 24 h and the coated foil was punched into circular disk. The cathode was  $60\ \mu\text{m}$  thick and it contained approximately  $5\text{--}7\ \text{mg cm}^{-2}$  of active material. The charge and discharge characteristics of the cathodes were examined using a coin cell (2032 type). The cell consisted of a cathode, electrolyte, a lithium metal anode, and a Celgard 2500 separator. The electrolyte was a 1 M  $\text{LiPF}_6$ -ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC) solution. The galvanostatic charge–discharge experiment was performed between 2.8 and 4.2 V using a Maccor 4000 battery cycler. EIS (electrochemical impedance spectroscopy) measurements of the cell at fully discharged state were carried out using a Schlumberger model SI 1260 impedance/gain-phase analyzer connected to a Schlumberger model SI 1286 electrochemical interface. The amplitude of the ac signal was 5 mV over the frequency range between 100 kHz and 10 mHz.

## 3. Results and discussion

### 3.1. Structure and morphology of the carbon-coated $\text{LiFePO}_4$

Fig. 1 shows XRD patterns of the bare (Fig. 1(a)) and the carbon-coated (Fig. 1(b)) olivine  $\text{LiFePO}_4$ . The XRD pattern of the bare  $\text{LiFePO}_4$  could be indexed as an orthorhombic sys-

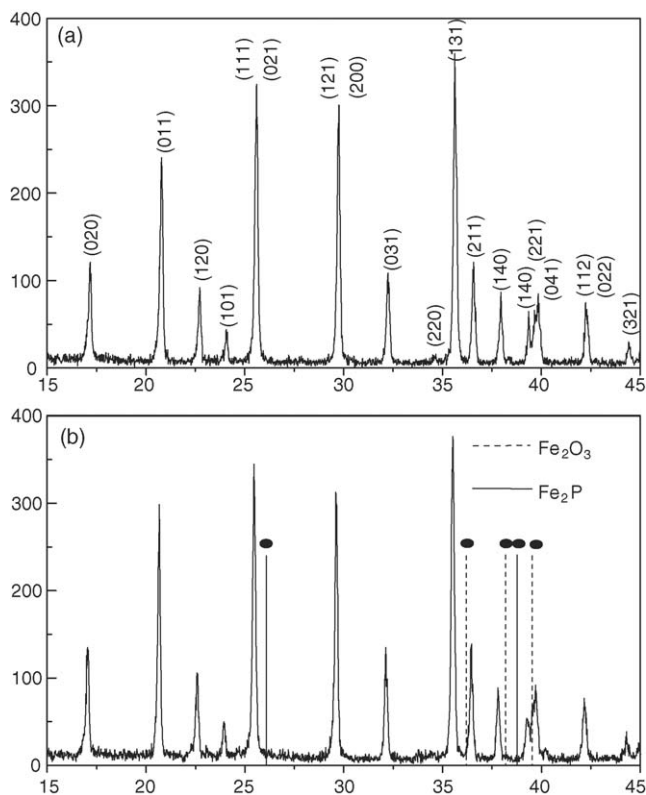


Fig. 1. XRD patterns of (a) the bare  $\text{LiFePO}_4$  and (b) the carbon-coated  $\text{LiFePO}_4$  after heat treatment at  $700^\circ\text{C}$  for 10 h.

tem (space group  $Pnmb$ ). Noticeable structural changes were not observed in the XRD pattern of the carbon-coated  $\text{LiFePO}_4$  indicating that the olivine structure was well maintained after carbon coating. Impurity phases such as  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_2\text{P}$ , which were reported by others [12,18], were not observed in the carbon-coated  $\text{LiFePO}_4$ .

Fig. 2 shows SEM images of the bare (Fig. 2(a)) and the carbon-coated (Fig. 2(b))  $\text{LiFePO}_4$  particles. It showed that the carbon-coated  $\text{LiFePO}_4$  was consisted of non-uniform fine particles with the size ranged between 100 and 300 nm. The size of the carbon-coated  $\text{LiFePO}_4$  particle was much smaller than that for the bare  $\text{LiFePO}_4$ . This indicated that the addition of carbon inhibited the particle growth during a sintering. A similar result was reported by Huang et al. [10] suggesting that the addition of fine carbon to the precursors reduced the particle size of the  $\text{LiFePO}_4$ . Prosini et al. [9] and Chen and Dahn [11] also showed that the particle size decreased as the amount of carbon increased.

Fig. 3 shows HRTEM bright field images of the bare  $\text{LiFePO}_4$  (Fig. 3(a)) and the carbon-coated  $\text{LiFePO}_4$  (Fig. 3(b)). The carbon-coated particles showed that the coating was not uniform and the thickness of carbon on the particle was in the range of several nanometer, suggesting that the carbon played an important role in reducing the  $\text{LiFePO}_4$  particle size during synthesis process. This result was similar to the previous ones [9–11] and it indicated that the carbon covering the  $\text{LiFePO}_4$  particle prevented the growth of the  $\text{LiFePO}_4$  particles by impeding diffusion during heat-treatments.

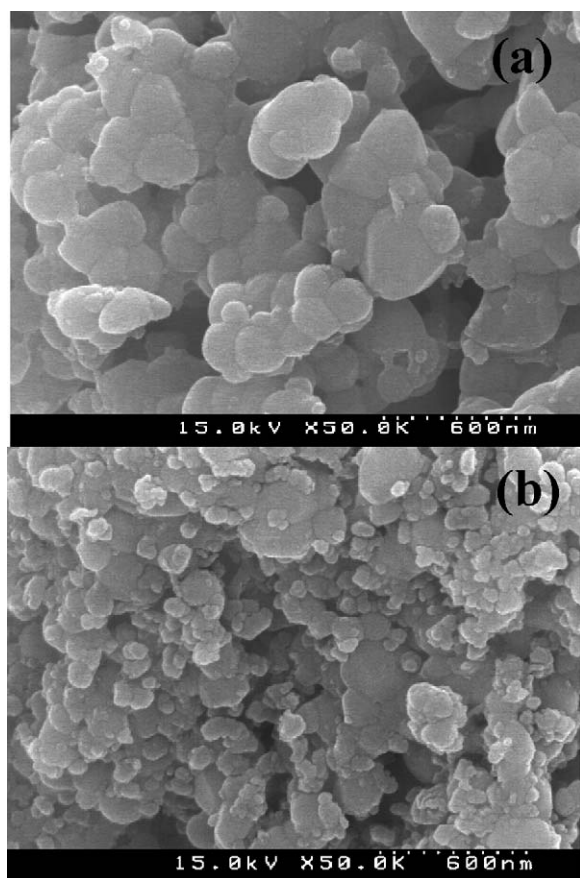


Fig. 2. SEM micrographs of (a) the bare and (b) the carbon-coated LiFePO<sub>4</sub> particles.

### 3.2. Electrochemical properties of the carbon-coated LiFePO<sub>4</sub>

Electrochemical performance of the carbon-coated LiFePO<sub>4</sub> was examined by charge–discharge tests and cyclic voltammetry. The cell was cycled between 2.8 and 4.2 V and charged at 0.1 C. Excellent electrochemical properties were obtained by using the carbon-coated LiFePO<sub>4</sub> prepared in this study (Fig. 4). The charge–discharge curves showed flat voltage plateaus at 3.4–3.5 V range, indicating two-phase nature of lithium extraction and insertion reactions between LiFePO<sub>4</sub> and FePO<sub>4</sub> [1]. Fig. 4 also showed different voltage profiles at different discharge rates. The specific capacity was 150 mAh g<sup>-1</sup> at 0.05 C and the plateau voltage and the specific discharge capacity decreased as the discharge current density increased. The discharge voltage plateaus were maintained at constant values regardless of discharge current density. When the carbon-coated LiFePO<sub>4</sub> was used, the cell delivered a capacity of 135 mAh g<sup>-1</sup> with a plateau at 3.3 V versus Li/Li<sup>+</sup> at the high discharge rate of 1 C. At low discharge rates, on the other hand, small voltage differences between charge and discharge plateaus were obtained, indicating its enhanced kinetics of the carbon-coated LiFePO<sub>4</sub> during electrochemical process comprising diffusion of lithium ions and electron transfer [19].

The carbon coating effect on the electrochemical properties of the LiFePO<sub>4</sub> was also supported by cyclic voltammetry shown

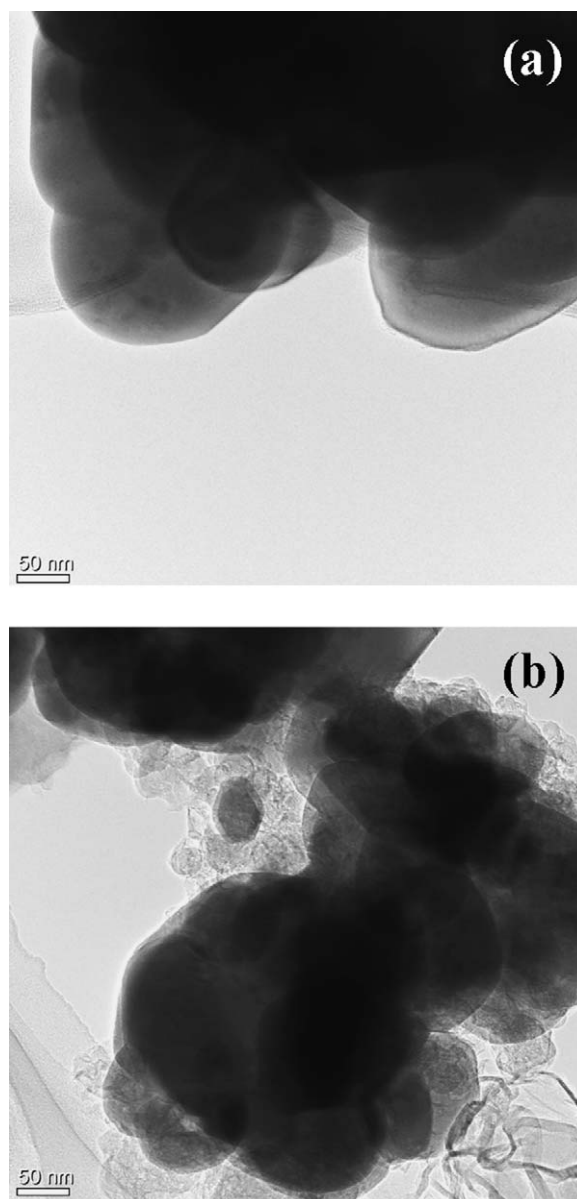


Fig. 3. TEM images of (a) the bare and (b) the carbon-coated LiFePO<sub>4</sub> particles.

in Fig. 5. The voltage differences of the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub> exhibited almost same intervals. However, anodic and cathodic peak intensities of the carbon-coated LiFePO<sub>4</sub> were much larger than those of the bare LiFePO<sub>4</sub>. This indicated that Li-ions and electrons were participating actively in redox reactions due to the carbon coating of the LiFePO<sub>4</sub>, allowing reversible electrochemical reactions during extraction and insertion of Li ions.

The cycling performance of the bare and the carbon-coated LiFePO<sub>4</sub> was described in Fig. 6. It showed capacity values from both discharge and charge stages as a function of cycle number. It indicated that the irreversible capacity was very small at each cycle (0.1–0.3 mAh g<sup>-1</sup>), except initial two cycles. However, the figure clearly showed that the capacity of the bare LiFePO<sub>4</sub> was decreased much faster than the carbon-coated LiFePO<sub>4</sub> during the cycle tests. The rapid capacity fading of the bare LiFePO<sub>4</sub>

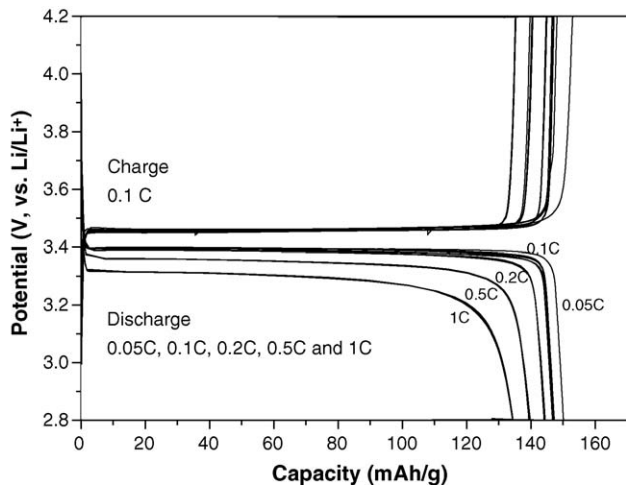


Fig. 4. Charge–discharge curves of the carbon-coated LiFePO<sub>4</sub> at different discharge rates. Specific charge current was 15 mA g<sup>-1</sup> at 0.1 C.

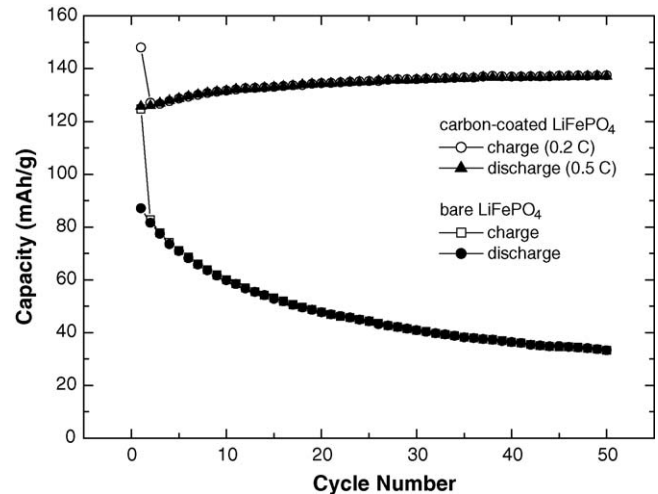


Fig. 6. Cycling performance of the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub>.

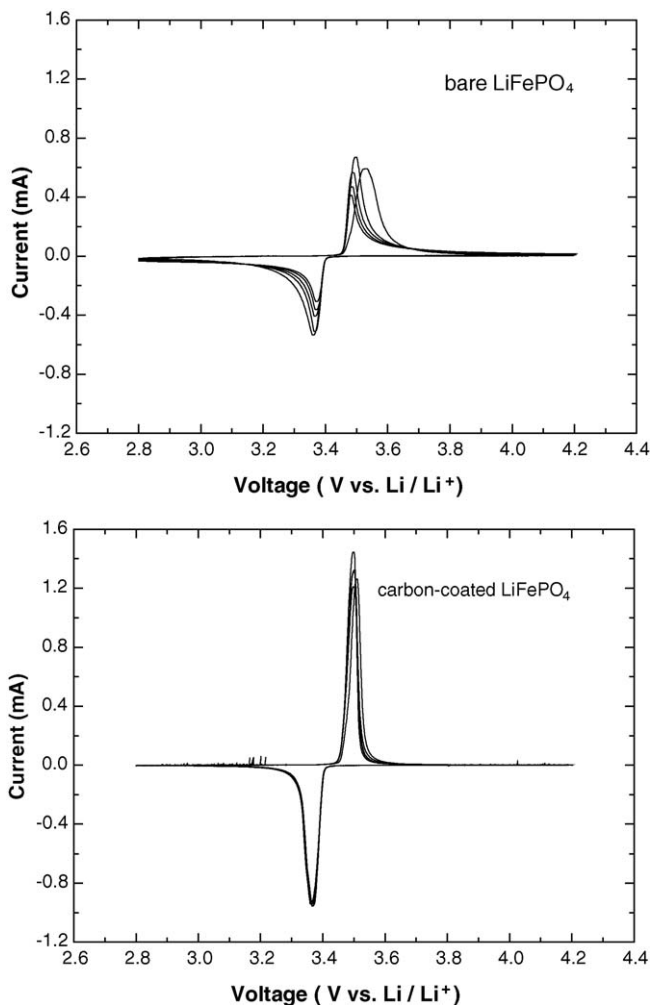


Fig. 5. Cyclic voltammograms of the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub> at a scan rate of 0.01 mV s<sup>-1</sup>.

was ascribed to the two-phase redox reactions, which was associated to the reduction of charge capacity of LiFePO<sub>4</sub> particles. On the contrary, the carbon-coated LiFePO<sub>4</sub> exhibited excellent capacity retention without capacity fading. The reversible capacity was approximately 140 mAh g<sup>-1</sup> at 0.5 C.

To understand the carbon coating effect in depth, ac impedance measurement was carried out using the cells containing the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub>. For the stable SEI film formation and the percolation of electrolyte through electrode particles, impedance measurement was carried out after performing galvanostatical cycles for five times. Impedance was also measured after 10 and 30 cycles. Fig. 7 shows Nyquist plots obtained from the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub> electrodes after 5th, 10th, and 30th cycle tests. An intercept at the  $Z_{\text{real}}$  axis in high frequency corresponded to the ohmic resistance ( $R_{\Omega}$ ), which represented the total resistance of the electrolyte, separator, and electrical contacts. The depressed semicircle in the high frequency range was related to the Li-ion migration resistance ( $R_f$ ) through the SEI film formed on the electrode or another coating layer. Second semicircle in the middle frequency range indicated the charge transfer resistance ( $R_{ct}$ ). The inclined line in the lower frequency represented the Warburg impedance, which was associated with lithium-ion diffusion in the LiFePO<sub>4</sub> particles. Simplified equivalent circuits models were constructed to analyze the impedance spectra (Fig. 8). Table 1 shows the parameters of the equivalent circuit for the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub> by

Table 1  
Impedance parameters calculated from equivalent circuits

Cathode electrode	Cycles	$R_{\Omega}$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
Bare LiFePO <sub>4</sub>	5	5.184	228.5	493.3
	10	5.69	245.4	1650
	30	22.09	255.7	8614
Carbon-coated LiFePO <sub>4</sub>	5	4.23	20.59	9.253
	10	4.42	21.7	11.44
	30	4.479	25.77	12.39



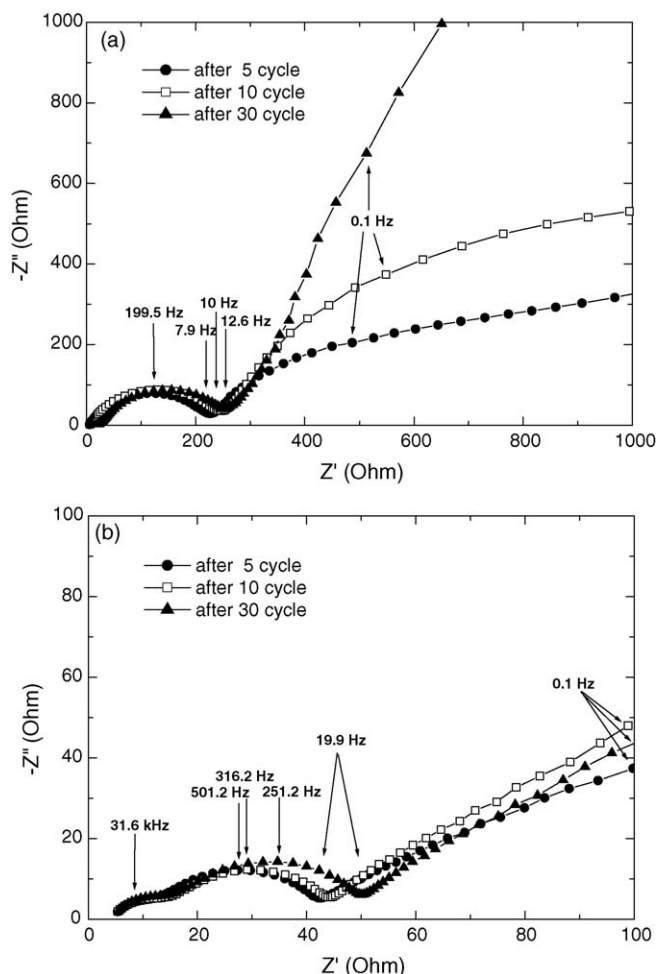


Fig. 7. EIS plots of the cells containing (a) the bare and (b) the carbon-coated LiFePO<sub>4</sub> electrodes in the discharged state.

computer simulations (Z-Plot<sup>®</sup>). It showed that the values of  $R_f$  and  $R_{ct}$  of the carbon-coated LiFePO<sub>4</sub> electrode were reduced comparing to the bare LiFePO<sub>4</sub> electrode, explaining the higher initial capacity of carbon-coated LiFePO<sub>4</sub> electrode in Fig. 6. In particular, the charge transfer resistance of the bare LiFePO<sub>4</sub> electrode increased drastically from 493.3 to 8614  $\Omega$  after 30 cycles, while  $R_{ct}$  of the carbon-coated LiFePO<sub>4</sub> electrode did not change much. Table 1 also shows that  $R_f$  values were decreased by coating the LiFePO<sub>4</sub> with carbon, suggesting that the resistance of Li-ion migration was decreased. On the other hand, the  $R_f$  values were not changed by extended cycling tests, suggesting that the carbon changed the electrochemical properties of SEI but the SEI played a major role in determining the initial capacity of the LiFePO<sub>4</sub> electrode but did not affect the capacity retention of the cathode.

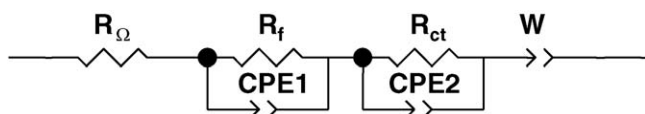


Fig. 8. An equivalent circuit for the bare LiFePO<sub>4</sub> and the carbon-coated LiFePO<sub>4</sub> to fit impedance data.

The improved electrochemical properties of the carbon-coated LiFePO<sub>4</sub>, therefore, appeared due to two factors. One was the reduced size of carbon-coated LiFePO<sub>4</sub> particles, which shortened the distance of the diffusion path for Li ions. The other was the improved electrical conductivity of the cathode since the carbon in the LiFePO<sub>4</sub> provided good electrical contacts between the LiFePO<sub>4</sub> particles and the conductor in the cathode composite.

#### 4. Conclusions

Electrochemical properties of the carbon-coated LiFePO<sub>4</sub>, which was synthesized by mechanochemical activation method, were investigated. The carbon-coated LiFePO<sub>4</sub> particles showed the olivine structure and the size of the particles were significantly reduced by the addition of carbon. HRTEM images revealed that the carbon layer on the carbon-coated LiFePO<sub>4</sub> particles were non-uniform and it was several nanometer thick. The electrochemical performance of the carbon-coated LiFePO<sub>4</sub> showed higher specific capacity and better capacity retention compared to the bare LiFePO<sub>4</sub>. At room temperature, the carbon-coated cathode showed stable capacity of 150 mAh g<sup>-1</sup> at 0.05 C and 135 mAh g<sup>-1</sup> at 1 C. It was confirmed that the carbon coating of the LiFePO<sub>4</sub> particles decreased the resistances of Li-ion migration and charge transfer from CV and ac impedance measurements. The improved capacity retention during cycle tests was attributed to the reduced LiFePO<sub>4</sub> particle size and enhanced electrical contacts by carbon.

#### Acknowledgement

This work was supported by the Core Technology Development Program of the Ministry of Commerce, Industry and Energy (MOCIE).

#### References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] D.D. MacNeil, Z. Lu, Z. Chen, J.R. Dahn, *J. Power Sources* 108 (2002) 8.
- [3] M. Takahashi, S.I. Tobishima, K. Takei, Y. Sakurai, *Solid State Ionics* 148 (2002) 283.
- [4] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1609.
- [5] M. Takahashi, S. Tobishima, K. Takei, Y. Sakurai, *J. Power Sources* 97/98 (2001) 508.
- [6] J. Barker, M.Y. Saidi, J.L. Swoyer, *Electrochem. Solid-State Lett.* 6 (2003) A53.
- [7] A.S. Andersson, B. Kalska, L. Haggstrom, J.O. Thomas, *Solid State Ionics* 130 (2000) 41.
- [8] N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, *J. Power Sources* 97/98 (2001) 503.
- [9] P.P. Prosini, D. Zane, M. Pasquali, *Electrochim. Acta* 46 (2001) 3517.
- [10] H. Huang, S.C. Yin, L.F. Nazar, *Electrochem. Solid-State Lett.* 4 (2001) A170.
- [11] Z. Chen, J.R. Dahn, *J. Electrochem. Soc.* 149 (2002) A1184.
- [12] S.Y. Chung, J.T. Bloking, Y.M. Chiang, *Nat. Mater.* 1 (2002) 123.
- [13] S. Shi, L. Liu, C. Ouyang, D.S. Wang, Z. Wang, L. Chen, X. Huang, *Phys. Rev. B* 68 (2003) 195108.

- [14] D. Wang, H. Li, S. Shi, X. Huang, L. Chen, *Electrochem. Acta* 50 (2005) 2955.
- [15] A. Yamada, S.C. Chung, K. Hinokuma, *J. Electrochem. Soc.* 148 (2001) A224.
- [16] H.S. Kim, B.W. Cho, W.I. Cho, *J. Power Sources* 132 (2004) 235.
- [17] S. Franger, F.L. Cras, C. Bourbon, H. Rouault, *J. Power Sources* 119–121 (2003) 252.
- [18] S.J. Kwon, C.W. Kim, W.T. Jeong, K.S. Lee, *J. Power Sources* 137 (2004) 93.
- [19] C.H. Mi, X.B. Zhao, G.S. Cao, J.P. Tu, *J. Electrochem. Soc.* 152 (2005) 483.